



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/GB99/00292 <b>(22) International Filing Date:</b> 28 January 1999 (28.01.99) <b>(30) Priority Data:</b> 9802504.2 6 February 1998 (06.02.98) GB <b>(71) Applicant (for all designated States except US):</b> JOHNSON MATTHEY PUBLIC LIMITED COMPANY [GB/GB]; 2-4 Cockspur Street, Trafalgar Square, London SW1Y 5BQ (GB). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> ANDREASSON, Anders [SE/SE]; Traneredsvagen 60 A, S-426 77 V. Frolunda (SE). CHANDLER, Guy, Richard [GB/GB]; 48 Harlton Road, Little Eversden, Cambridge CB3 7HB (GB). GÖRSMANN, Claus, Friedrich [DE/GB]; 39 Cromwell Road, Cambridge CB1 3EB (GB). WARREN, James, Patrick [GB/GB]; 67 Burnside, Cambridge CB1 3PA (GB). <b>(74) Agent:</b> WISHART, Ian, Carmichael; Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading RG4 9NH (GB).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> SYSTEM FOR NO <sub>x</sub> REDUCTION IN EXHAUST GASES  <b>(57) Abstract</b>  A system for NO <sub>x</sub> reduction in combustion gases, especially from diesel engines, incorporates an oxidation catalyst to convert at least a portion of NO to NO <sub>2</sub> , a particulate filter, a source of reductant such as NH <sub>3</sub> , and an SCR catalyst. Considerable improvements in NO <sub>x</sub> conversion are observed.		

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SYSTEM FOR NO<sub>x</sub> REDUCTION IN EXHAUST GASES

The present invention concerns improvements in selective catalytic reduction of NO<sub>x</sub> in waste gas streams such as diesel engine exhausts or other lean exhaust gases such as from gasoline direct injection (GDI).

The technique named SCR (Selective Catalytic Reduction) is well established for industrial plant combustion gases, and may be broadly described as passing a hot exhaust gas over a catalyst in the presence of a nitrogenous reductant, especially ammonia or urea. This is effective to reduce the NO<sub>x</sub> content of the exhaust gases by about 20-25% at about 250°C, or possibly rather higher using a platinum catalyst, although platinum catalysts tend to oxidise NH<sub>3</sub> to NO<sub>x</sub> during higher temperature operation. We believe that SCR systems have been proposed for NO<sub>x</sub> reduction for vehicle engine exhausts, especially large or heavy duty diesel engines, but this does require on-board storage of such reductants, and is not believed to have met with commercial acceptability at this time.

We believe that if there could be a significant improvement in performance of SCR systems, they would find wider usage and may be introduced into vehicular applications. It is an aim of the present invention to improve significantly the conversion of NO<sub>x</sub> in a SCR system, and to improve the control of other pollutants using a SCR system.

Accordingly, the present invention provides an improved SCR catalyst system, comprising in combination and in order, an oxidation catalyst effective to convert NO to NO<sub>2</sub>, a particulate filter, a source of reductant fluid and downstream of said source, an SCR catalyst.

The invention further provides an improved method of reducing NO<sub>x</sub> in gas streams containing NO and particulates comprising passing such gas stream over an oxidation catalyst under conditions effective to convert at least a portion of NO in the gas stream to NO<sub>2</sub>, removing at least a portion of said particulates, adding reductant fluid to the gas stream containing enhanced NO<sub>2</sub> to form a gas mixture, and passing the gas mixture over an SCR catalyst.

Although the present invention provides, at least in its preferred embodiments, the opportunity to reduce very significantly the NO<sub>x</sub> emissions from the lean (high in oxygen) exhaust gases from diesel and similar engines, it is to be noted that the invention also permits very good reductions in the levels of other regulated pollutants, especially hydrocarbons and particulates.

The invention is believed to have particular application to the exhausts from heavy duty diesel engines, especially vehicle engines, eg truck or bus engines, but is not to be regarded as being limited thereto. Other applications might be LDD (light duty diesel), GDI, CNG (compressed natural gas) engines, ships or stationary sources. For simplicity, however, the majority of this description concerns such vehicle engines.

We have surprisingly found that a "pre-oxidising" step, which is not generally considered necessary because of the low content of CO and unburnt fuel in diesel exhausts, is particularly effective in increasing the conversion of NO<sub>x</sub> to N<sub>2</sub> by the SCR system. We also believe that minimising the levels of hydrocarbons in the gases may assist in the conversion of NO to NO<sub>2</sub>. This may be achieved catalytically and/or by engine design or management. Desirably, the NO<sub>2</sub>/NO ratio is adjusted according to the present invention to the most beneficial such ratio for the particular SCR catalyst and CO and hydrocarbons are oxidized prior to the SCR catalyst. Thus, our preliminary results indicate that for a transition metal/zeolite SCR catalyst it is desirable to convert all NO to NO<sub>2</sub>, whereas for a rare earth-based SCR catalyst, a high ratio is desirable providing there is some NO, and for other transition metal-based catalysts gas mixtures are notably better than either substantially only NO or NO<sub>2</sub>. Even more surprisingly, the incorporation of a particulate filter permits still higher conversions of NO<sub>x</sub>.

The oxidation catalyst may be any suitable catalyst, and is generally available to those skilled in art. For example, a Pt catalyst deposited upon a ceramic or metal through-flow honeycomb support is particularly suitable. Suitable catalysts are e.g. Pt/Al<sub>2</sub>O<sub>3</sub> catalysts, containing 1-150g Pt/ft<sup>3</sup> (0.035-5.3g Pt/litre) catalyst volume depending on the

NO<sub>2</sub>/NO ratio required. Such catalysts may contain other components providing there is a beneficial effect or at least no significant adverse effect.

5 The source of reductant fluid conveniently uses existing technology to inject fluid into the gas stream. For example, in the tests for the present invention, a mass controller was used to control supply of compressed NH<sub>3</sub>, which was injected through an annular injector ring mounted in the exhaust pipe. The injector ring had a plurality of injection ports arranged around its periphery. A conventional diesel fuel injection system including pump and injector nozzle has been used to inject urea by the present applicants. A stream of  
10 compressed air was also injected around the nozzle; this provided good mixing and cooling.

The reductant fluid is suitably NH<sub>3</sub>, but other reductant fluids including urea, ammonium carbamate and hydrocarbons including diesel fuel may also be considered. Diesel fuel is, of course, carried on board a diesel-powered vehicle, but diesel fuel itself is  
15 a less selective reductant than NH<sub>3</sub> and is presently not preferred.

Suitable SCR catalysts are available in the art and include Cu-based and vanadia-based catalysts. A preferred catalyst at present is a V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>/TiO<sub>2</sub> catalyst, supported on a honeycomb through-flow support. Although such a catalyst has shown good performance  
20 in the tests described hereafter and is commercially available, we have found that sustained high temperature operation can cause catalyst deactivation. Heavy duty diesel engines, which are almost exclusively turbocharged, can produce exhaust gases at greater than 500°C under conditions of high load and/or high speed, and such temperatures are sufficient to cause catalyst deactivation. In one embodiment of the invention, therefore, cooling means  
25 is provided upstream of the SCR catalyst. Cooling means may suitably be activated by sensing high catalyst temperatures or by other, less direct, means, such as determining conditions likely to lead to high catalyst temperatures. Suitable cooling means include water injection upstream of the SCR catalyst, or air injection, for example utilising the engine turbocharger to provide a stream of fresh intake air by-passing the engine. We have  
30 observed a loss of activity of the catalyst, however, using water injection, and air injection by modifying the turbocharger leads to higher space velocity over the catalyst which tends

to reduce NOx conversion. Preferably, the preferred SCR catalyst is maintained at a temperature from 160°C to 450°C.

We believe that in its presently preferred embodiments, the present invention may depend upon an incomplete conversion of NO to NO<sub>2</sub>. Desirably, therefore, the oxidation catalyst, or the oxidation catalyst together with the particulate trap if used, yields a gas stream entering the SCR catalyst having a ratio of NO to NO<sub>2</sub> of from about 4:1 to about 1:3 by vol, for the commercial vanadia-type catalyst. As mentioned above, other SCR catalysts perform better with different NO/NO<sub>2</sub> ratios. We do not believe that it has previously been suggested to adjust the NO/NO<sub>2</sub> ratio in order to improve NOx reduction.

The present invention incorporates a particulate trap downstream of the oxidation catalyst. We discovered that soot-type particulates may be removed from a particulate trap by "combustion" at relatively low temperatures in the presence of NO<sub>2</sub>. In effect, the incorporation of such a particulate trap serves to clean the exhaust gas of particulates without causing accumulation, with resultant blockage or back-pressure problems, whilst simultaneously reducing a proportion of the NOx. Suitable particulate traps are generally available, and are desirably of the type known as wall-flow filters, generally manufactured from a ceramic, but other designs of particulate trap, including woven knitted or non-woven heat-resistant fabrics, may be used.

It may be desirable to incorporate a clean-up catalyst downstream of the SCR catalyst, to remove any NH<sub>3</sub> or derivatives thereof which could pass through unreacted or as by-products. Suitable clean-up catalysts are available to the skilled person.

A particularly interesting possibility arising from the present invention has especial application to light duty diesel engines (car and utility vehicles) and permits a significant reduction in volume and weight of the exhaust gas after-treatment system, in a suitable engineered system.

Several tests have been carried out in making the present invention. These are described below, and are supported by results shown in graphical form in the attached drawings.

- 5           A commercial 10 litre turbocharged heavy duty diesel engine on a test-bed was used for all the tests described herein.

#### **Test 1 - (Comparative)**

- 10           A conventional SCR system using a commercial  $V_2O_5/WO_3/TiO_2$  catalyst, was adapted and fitted to the exhaust system of the engine.  $NH_3$  was injected upstream of the SCR catalyst at varying ratios. The  $NH_3$  was supplied from a cylinder of compressed gas and a conventional mass flow controller used to control the flow of  $NH_3$  gas to an experimental injection ring. The injection ring was a 10cm diameter annular ring provided  
15           with 20 small injection ports arranged to inject gas in the direction of the exhaust gas flow.  $NO_x$  conversions were determined by fitting a  $NO_x$  analyser before and after the SCR catalyst and are plotted against exhaust gas temperature in Figure 1. Temperatures were altered by maintaining the engine speed constant and altering the torque applied.

- 20           A number of tests were run at different quantities of  $NH_3$  injection, from 60% to 100% of theoretical, calculated at 1:1  $NH_3/NO$  and 4:3  $NH_3/NO_2$ . It can readily be seen that at low temperatures, corresponding to light load, conversions are about 25%, and the highest conversions require stoichiometric (100%) addition of  $NH_3$  at catalyst temperatures of from 325 to 400°C, and reach about 90%. However, we have determined that at greater than  
25           about 70% of stoichiometric  $NH_3$  injection,  $NH_3$  slips through the SCR catalyst unreacted, and can cause further pollution problems.

#### **Test 2 (Comparative)**

- 30           The test rig was modified by inserting into the exhaust pipe upstream of the  $NH_3$  injection, a commercial platinum oxidation catalyst of 10.5 inch diameter and 6 inch length

(26.67cm diameter and 15.24cm length) containing 10g Pt/ft<sup>3</sup> (= 0.35g/litre) of catalyst volume. Identical tests were run, and it was observed from the results plotted in Figure 2, that even at 225°C, the conversion of NOx has increased from 25% to >60%. The greatest conversions were in excess of 95%. No slippage of NH<sub>3</sub> was observed in this test nor in the following test.

### Test 3

The test rig was modified further, by inserting a particulate trap before the NH<sub>3</sub> injection point, and the tests run again under the same conditions at 100% NH<sub>3</sub> injection and a space velocity in the range 40,000 to 70,000 hr<sup>-1</sup> over the SCR catalyst. The results are plotted and shown in Figure 3. Surprisingly, there is a dramatic improvement in NOx conversion, to above 90% at 225°C, and reaching 100% at 350°C. Additionally, of course, the particulates which are the most visible pollutant from diesel engines, are also controlled.

### Test 4

An R49 test with 80% NH<sub>3</sub> injection was carried out over a V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>/TiO<sub>2</sub> SCR catalyst. This gave 67% particulate, 89% HC and 87% NOx conversion; the results are plotted in Figure 4.

Additionally tests have been carried out with a different diesel engine, and the excellent results illustrated in Test 3 and 4 above have been confirmed.

The results have been confirmed also for a non-vanadium SCR catalyst.



**CLAIMS**

1. An improved SCR system for treating combustion exhaust gas containing NO and particulates, comprising in combination and in order, an oxidation catalyst effective to  
5 convert at least a portion of NO in said NO<sub>x</sub> to NO<sub>2</sub>, a particulate trap, a source of reductant fluid and an SCR catalyst.
2. An SCR system according to claim 1, wherein the reductant fluid is NH<sub>3</sub>.
- 10 3. An SCR system according to claim 1 or 2, wherein the oxidation catalyst is a platinum catalyst carried on a through-flow honeycomb support.
4. An SCR system according to claims 1,2 or 3 wherein the particulate filter is a wall-flow filter.
- 15 5. An SCR system according to any one of the preceding claims, comprising also means to cool gases upstream of the SCR catalyst.
6. An SCR system according to claim 5, comprising also control means such that said  
20 gas cooling means is activated only when a high SCR catalyst temperature is detected or conditions are determined that are expected to lead to high catalyst temperatures.
7. A diesel engine provided with an SCR system according to any one of claims 1 to 5.
- 25 8. A light duty diesel engine according to claim 6, wherein the volume of the exhaust gas after-treatment system is reduced. *exp.*
9. A method of reducing pollutants, including particulates and NO<sub>x</sub>, in gas streams, comprising passing such gas stream over an oxidation catalyst under conditions effective to  
30 convert at least a portion of NO in the gas stream to NO<sub>2</sub>, removing at least a portion of said

particulates, adding reductant fluid to the gas stream containing enhanced  $\text{NO}_2$  to form a gas mixture, and passing the gas mixture over an SCR catalyst under  $\text{NO}_x$  reduction conditions.

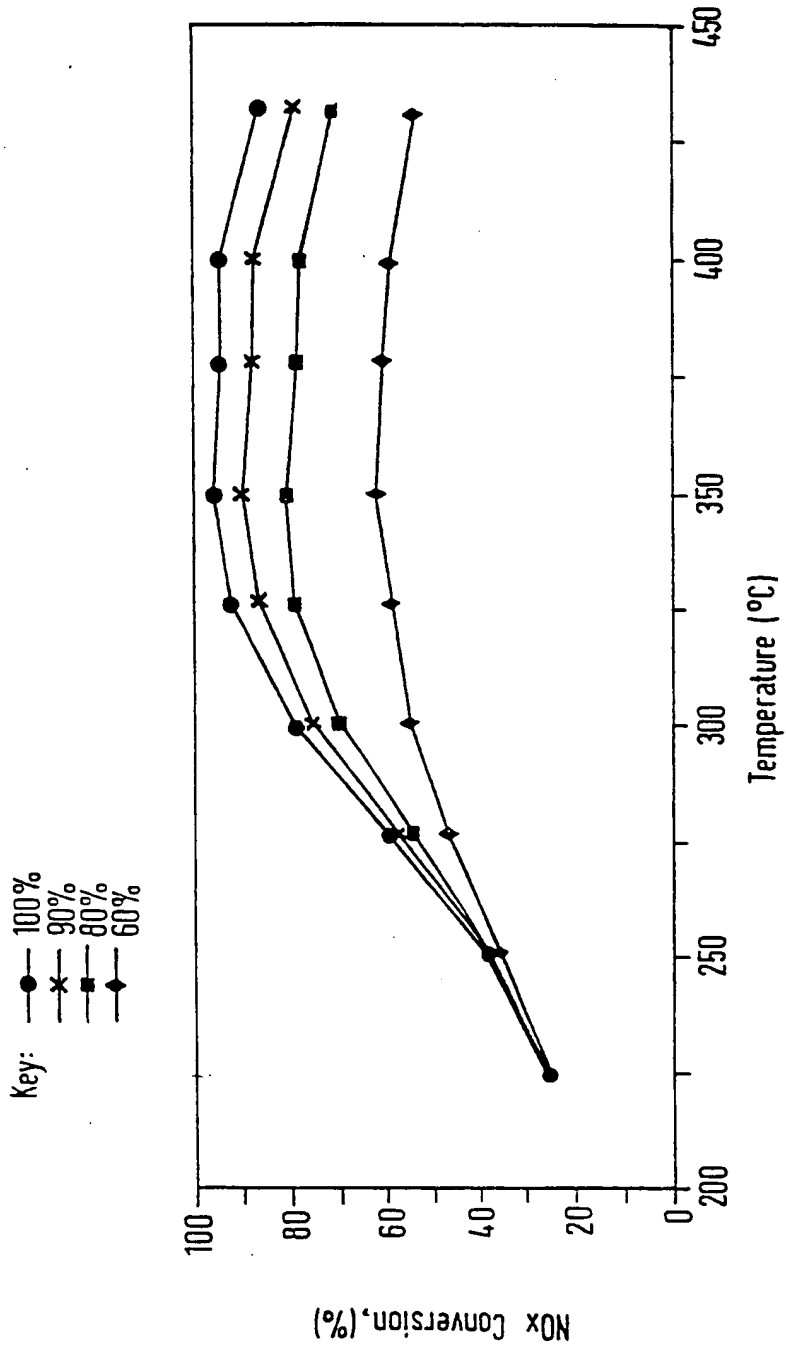
10. A method according to claim 9, wherein said gas stream is the exhaust from a diesel,  
5 GDI or CNG engine.

11. A method according to claim 9 or 10, wherein the gases are cooled, if necessary,  
before reaching the SCR catalyst.

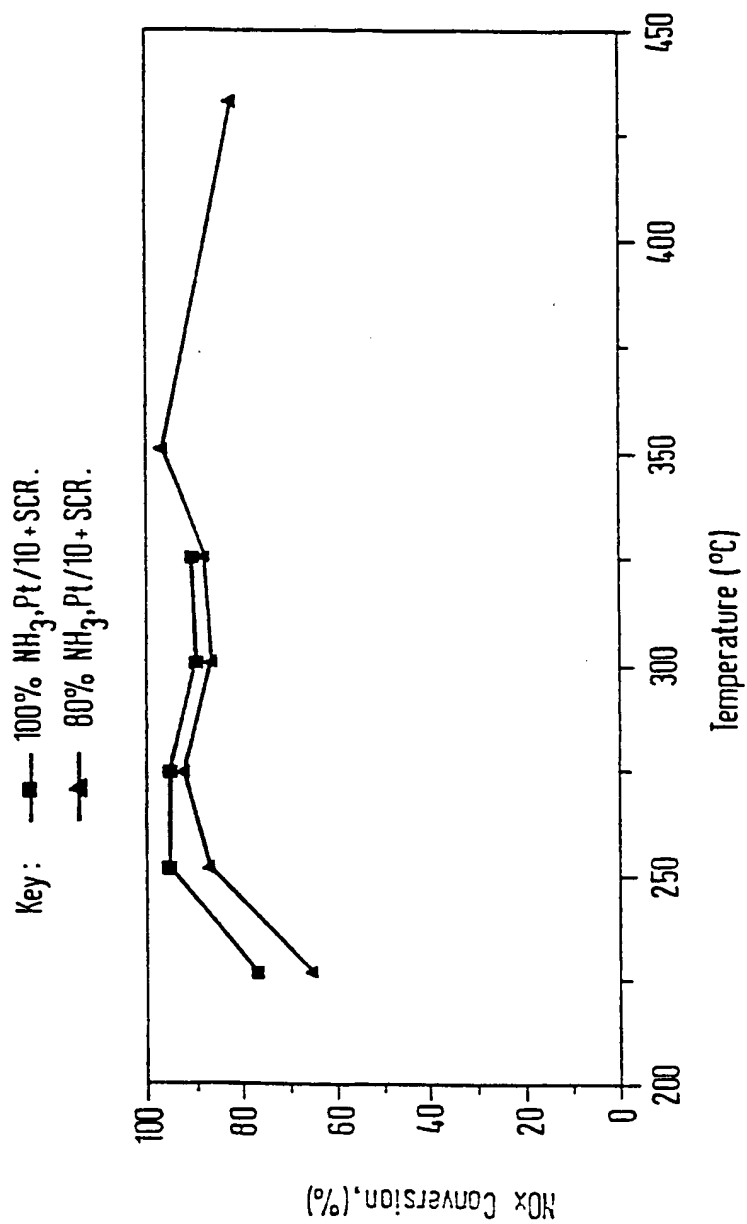
10 12. A method according to claim 9, 10 or 11, wherein the NO to  $\text{NO}_2$  ratio in the gases  
is adjusted to a level pre-determined to be optimum for the SCR catalyst, by oxidation of NO  
over an oxidation catalyst.

what is the  
optimum  
level

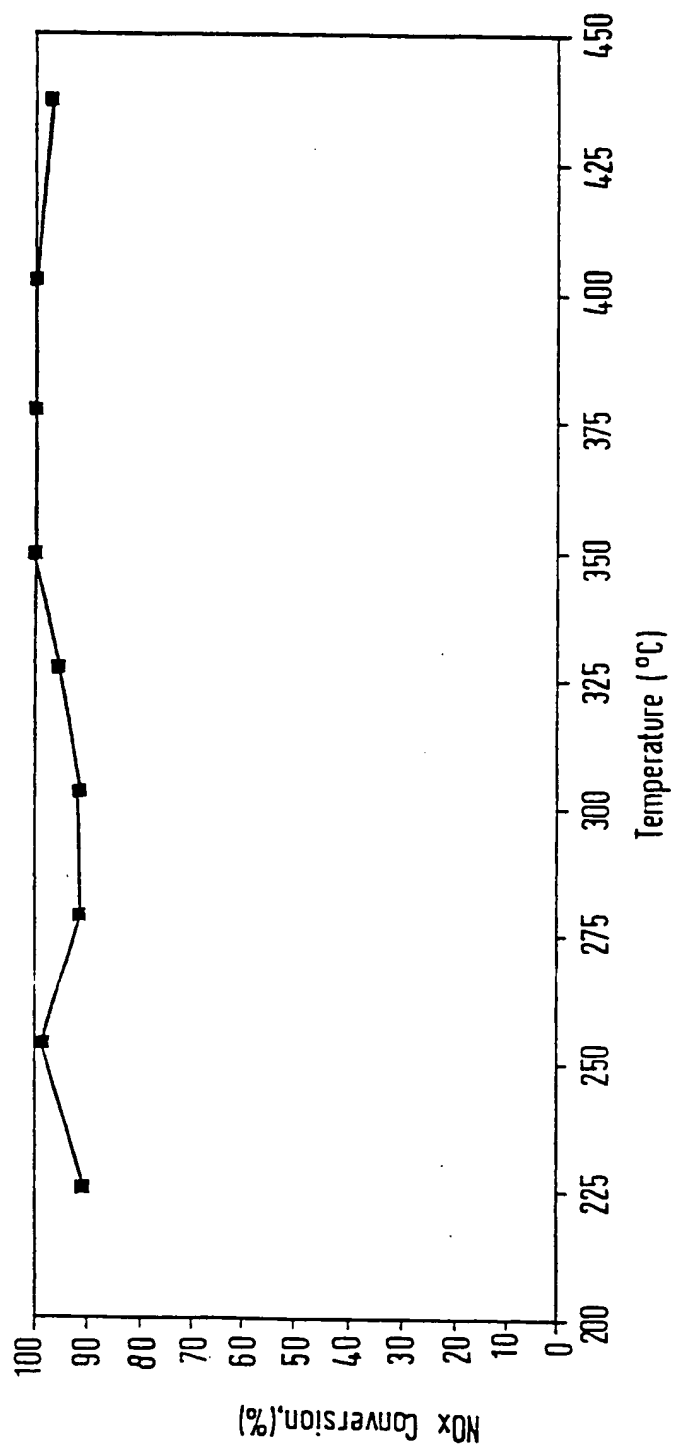
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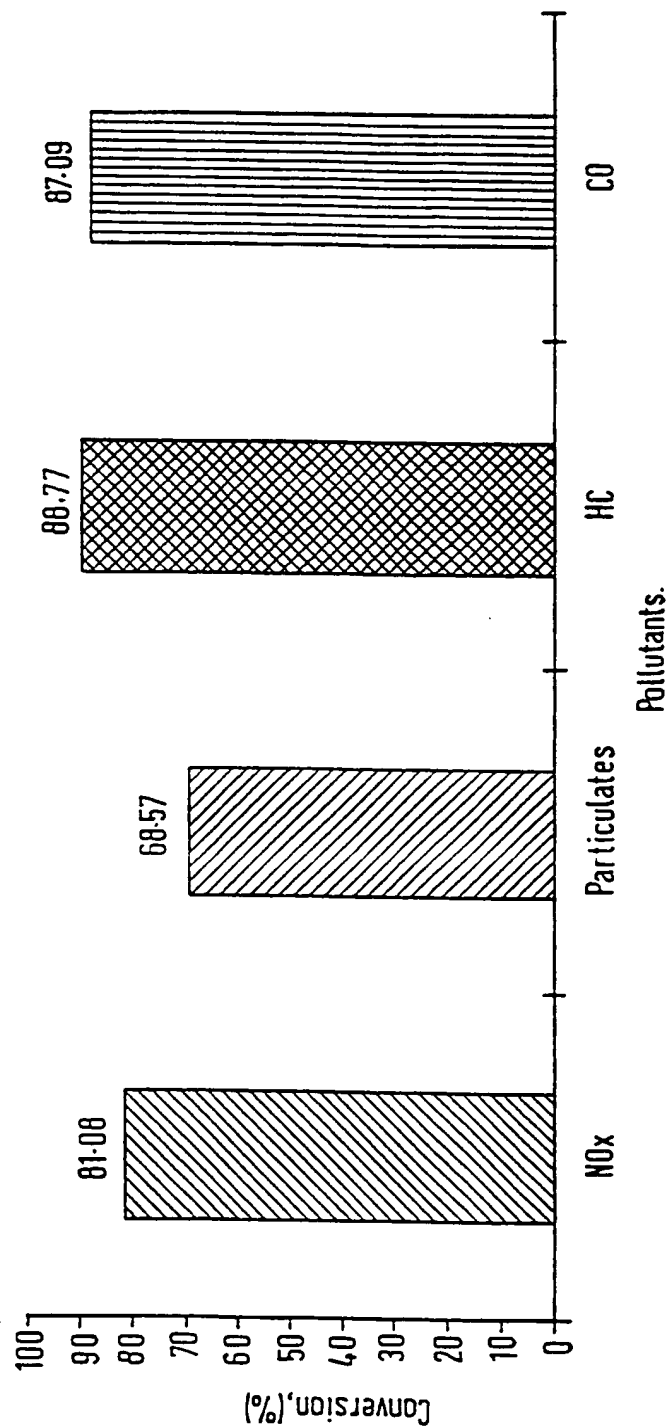


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# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 99/00292

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 B01D53/94 F01N3/28

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B01D F01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 758 713 A (TOYOTA MOTOR CO LTD) 19 February 1997 see column 2, line 34 - column 3, line 22 see column 16, line 33 - column 17, line 55; figure 6	1-4, 7, 9, 10, 12
Y	EP 0 283 913 A (GRACE W R & CO) 28 September 1988 see claims 1-35; figure 1	1-4, 7, 9, 10, 12
A	EP 0 341 832 A (JOHNSON MATTHEY INC) 15 November 1989 see claims 1-10; figure 1 - C/T -/-	1, 4, 7-9, 11, 12

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

International Application No

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI  Section Ch, Week 9710  Derwent Publications Ltd., London, GB;  Class H06, AN 97-104299  XP002102630  &amp; JP 08 338320 A (HINO MOTORS LTD)  , 24 December 1996  see abstract</p>	1,6-8,11
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Information on patent family members

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